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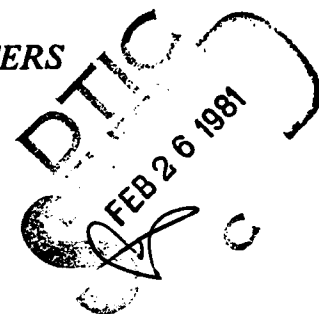
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THERMODYNAMIC ANALYSIS OF CHLOROALUMINATE
CONCENTRATION CELLS

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(6) THERMODYNAMIC ANALYSIS OF CHLOROALUMINATE CONCENTRATION CELLS,

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Equations are given for emf of concentration cells with chloroaluminate melts. The usual assumption that $t_{\text{M}} = 1$ may lead to doubtful interpretations, especially for melts with large organic cations.

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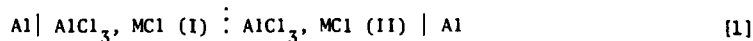
Chloroaluminate melts have attained great interest in later years in connection with the Alcoa smelting process and battery applications, and as a medium for unusual oxidation states, electrode reactions and organic reactions. The structure of chloroaluminate melts is summarized in Table 1.

TABLE 1
Species in Chloroaluminate Melts.

x_{AlCl_3}	0	0.50	0.667	1.00
Stoichiometric Composition	MCl	MAICl ₄	MA _{1/2} Cl ₇	AlCl ₃
Major melt species	M ⁺ Cl ⁻ , AlCl ₄ ⁻	M ⁺ AlCl ₄ ⁻ , Al ₂ Cl ₇ ⁻ (Al ₃ Cl ₁₀ ⁻), Al ₂ Cl ₆		

The most familiar chloroaluminate melts contain AlCl₃ in combination with NaCl or some other alkali metal chloride. Recently several studies have dealt with melts where a large organic cation has been substituted for the alkali ion, thus creating systems which are molten at or near room temperature.

A very common way of studying chloroaluminate melts is to make potentiometric measurements on the cell



to obtain thermodynamic information on activities or equilibria. As the relationship between emf and chemical potential is dependent on the transport properties of the melt, some assumptions have to be made. A typical statement taken from a recent potentiometric study of aluminum chloride - 1-butylpyridinium chloride (1) is: "The liquid junction potential at the

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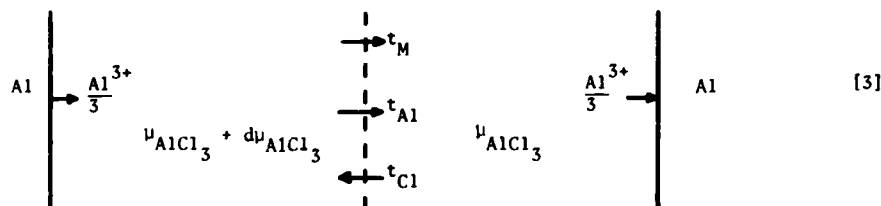
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Pyrex frit reference was neglected". The rationale for this assumption was made with reference to two early papers on AlCl_3 - NaCl mixtures (2,3). In these papers the probable but never proven assumption was made that Na^+ was the only charge carrier. The assumption that the cation is the only charge carrier may not be valid for a melt with an organic cation, which may well be significantly larger than AlCl_4^- . In fact, in two studies of the conductivities of several fused pyridinium halides (4,5) there was circumstantial evidence that the anions were important charge carriers. The concept of junction potential is also unnecessary and should be avoided as it leads to an artificial division of electrode and junction processes by introduction of an undefined single ion potential.

For a thermodynamic analysis of the concentration cell [1] we need not be concerned with structure, but may make a formalistic approach, setting the sum of the transport numbers of the constituents equal to 1:

$$t_{\text{Al}} + t_{\text{M}} + t_{\text{Cl}} = 1 \quad [2]$$

Let us then consider the passing of 1 Faraday through the concentration cell when the concentration difference is infinitesimally small:



It is readily seen that the emf is given by

$$-F dE = \frac{1}{3} d\mu_{\text{AlCl}_3} - \frac{t_{\text{Al}}}{3} d\mu_{\text{AlCl}_3} - t_{\text{M}} d\mu_{\text{MCl}} \quad [4]$$

when it is remembered that $t_{\text{Cl}} = 1 - t_{\text{Al}} - t_{\text{M}}$

Introduction of the Gibbs - Duhem relation

$$x_{\text{AlCl}_3} d\mu_{\text{AlCl}_3} + x_{\text{MCl}} d\mu_{\text{MCl}} = 0 \quad [5]$$

gives the final result

$$-F dE = \frac{(1 - t_{\text{Al}})(1 - x_{\text{AlCl}_3}) + 3 t_{\text{M}} x_{\text{AlCl}_3}}{3(1 - x_{\text{AlCl}_3})} d\mu_{\text{AlCl}_3} \quad [6]$$

If Cl_2 electrodes are used in the concentration cell [1] in place of aluminum, the emf is given by

$$-F dE = \frac{-t_{\text{Al}}(1 - x_{\text{AlCl}_3}) + 3 t_{\text{M}} x_{\text{AlCl}_3}}{3(1 - x_{\text{AlCl}_3})} d\mu_{\text{AlCl}_3} \quad [7]$$

Equations [6] and [7] give the emf in terms of the chemical potential of AlCl_3 and transport numbers without assumption or introduction of single ion potentials. If an artificial division between electrode and junction potentials should be made through introduction of single ion potential, Eqn. [4] shows that the processes occurring at the junction certainly cannot be neglected. Equation [6] may be straightforwardly applied if Al^{3+} , M^+ and Cl^- are the current

carriers, but it may also be used if AlCl_4^- or even Al_2Cl_7^- are current carriers through the membrane. If AlCl_4^- should be a current carrier aluminum would be transported from right to left, contrary to what is expected for Al^{3+} ions. Theoretically, both Al^{3+} and AlCl_4^- may transport the current at the same time. Although for the sake of illustration we implicitly have assumed transport with reference to a fixed membrane, this is an unnecessary assumption as only relative transport numbers are relevant for determination of emf. In the unlikely case that uncomplexed Al^{3+} should carry current we might still define that transport to be zero and hence set

$$t_{\text{Al}} = -3 t_{\text{AlCl}_4^-} \quad [8]$$

or if also Al_2Cl_7^- should carry current

$$t_{\text{Al}} = -3 t_{\text{AlCl}_4^-} - 6 t_{\text{Al}_2\text{Cl}_7^-} \quad [9]$$

In order to illustrate the relationship between emf, activity and transport properties the results for some limiting cases are given in Table 2 using Eqns. [6] and [9]. Included also are results at $x_{\text{AlCl}_3} = 0.50$, as many potentiometric studies are carried out close to this composition to obtain the equilibrium constant for the dissociation reaction



Most investigators (e.g., (2,3)) are using a model equivalent to model B in Table 2, although it may not straightforwardly be recognized as such. This model may be derived from Eqn. [4] with $t_M = 1$ and $t_{\text{Al}} = 0$

$$-F dE = \frac{1}{3} d\mu_{\text{AlCl}_3} - d\mu_{\text{MCl}} \quad [11]$$

$$0 = \frac{1}{3} d\mu_{\text{MCl}} - \frac{1}{3} d\mu_{\text{MCl}} \quad [12]$$

$$-F dE = \frac{1}{3} d\mu_{\text{MAAlCl}_4} - \frac{4}{3} d\mu_{\text{MCl}} \quad [13]$$

The assumption of $t_M = 1$ is probably the best available in view of the total lack of experimental determination of transport numbers. However, this assumption may only be true for the alkali chloroaluminate melts and is much less probable for the chloroaluminate melts with large organic cations. The most likely major current carrier in acidic melts with large organic cations is AlCl_4^- . It is then interesting to note from Table 2 that if only

$t_{\text{AlCl}_4^-} + t_M = 1$, i.e., no current carriers other than AlCl_4^- and M^+ (model F), then the emf would be the same as if only M^+ carried current for $x_{\text{AlCl}_3} = 0.50$.

Thus in spite of the fact that the argument of Gale and Osteryoung (1) probably is incorrect, their results may still be approximately correct. However, when the composition is different from 50 mol% AlCl_3 , it is no longer immaterial whether AlCl_4^- or M^+ carries the current. For example, the difference in $dE/d\mu_{\text{AlCl}_3}$ is already 16% at 55 mol% AlCl_3 .

Really serious errors in the transformation of emf data to activities and equilibrium constants will occur if Model B is used when Cl^- carries part of the current. Then the chemical potential may for instance be underestimated by a factor of 4 for $x_{\text{AlCl}_3} = 0.50$. In

TABLE 2

The Relationship between emf and Chemical Potential for Concentration Cell [1]
Making some Limiting Assumptions for Transport Numbers.

Model	Transport Numbers	$-FdE/d\mu_{\text{AlCl}_3}$	$-FdE/d\mu_{\text{AlCl}_3}$ ($x_{\text{AlCl}_3} = 0.50$)
A	$t_{\text{Al}} = 1$ ($t_{\text{M}} = t_{\text{Cl}} = 0$)	0	0
B	$t_{\text{M}} = 1$ ($t_{\text{Al}} = t_{\text{Cl}} = 0$)	$\frac{1 + 2 x_{\text{AlCl}_3}}{3 (1 - x_{\text{AlCl}_3})}$	$\frac{4}{3}$
C	$t_{\text{Cl}} = 1$ ($t_{\text{Al}} = t_{\text{M}} = 0$)	$\frac{1}{3}$	$\frac{1}{3}$
D	$t_{\text{AlCl}_4^-} = 1$ ($t_{\text{M}} = 0, t_{\text{Al}} = -3, t_{\text{Cl}} = 4$)	$\frac{4}{3}$	$\frac{4}{3}$
E	$t_{\text{Al}_2\text{Cl}_7^-} = 1$ ($t_{\text{M}} = 0, t_{\text{Al}} = -6, t_{\text{Cl}} = 7$)	$\frac{7}{3}$	$\frac{7}{3}$
F	$t_{\text{AlCl}_4^-} + t_{\text{M}} = 1$	$\frac{4}{3} - \frac{t_{\text{M}} (1 - 2 x_{\text{AlCl}_3})}{1 - x_{\text{AlCl}_3}}$	$\frac{4}{3}$

basic mixtures, especially with organic cations, Cl^- is a very likely current carrier candidate, and concentration cell studies in this range should be met with scepticism until transport numbers are known. One cannot totally exclude the possibility that Cl^- also may carry current in acid mixtures through a jump mechanism from one aluminum complex to another.

There is great need for the experimental determination of transport numbers in chloroaluminate melts, especially those with organic cations, in order to arrive at correct equilibrium constants from the many potentiometric studies that have been and are being made.

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